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The pairing relations for the magneto optical spectra of tetracene monovalent plus and minus ions

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reaction probability as $t \to \infty$.

This study supports the conclusion from our earlier work[1] that a cubic spline interpolation procedure is efficient enough to be employed in fitting *ab initio* potential-energy values. It also reveals that the error involved in the use of the splinefitted surface for a time-dependent QM study is less than that for the corresponding QT study as the former uses the more accurate function values rather than the less accurate first derivatives.

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The pairing relations for the magneto optical spectra of tetracene monovalent plus and minus ions

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In even alternant hydrocarbons, the pairing relations between bonding and antibonding molecular orbitals lead to identical absorption and electron spin resonance spectra for plus and minus ions of the same valency.[1] The constants A, B, and C used to characterize the magneto optical spectra have the same magnitudes but opposite signs for corresponding bands of the two ions.[2]

In a broad sense, the mirror resemblance of the magnetic circular dichroism (mcd) spectra of perylene plus and minus ions has recently been demonstrated.[3] It was found that small differences in the absorption spectra of both ions correspond to large deviations between the mcd spectra. Also, the effect of large overlap between absorption or mcd bands makes quantitative correlations more difficult. For these reasons we have measured the spectra of the positive and negative ions of tetracene. These ions can easily be prepared,[3] and the spectra show a larger number of well separated absorption bands in the region between 2000 and 6000 Å. Also the rather strong similarity between the absorption spectra of corresponding plus and minus ions suggested a better starting point for the mcd studies.

Both, monovalent and divalent ions, were measured. In the latter case the mcd was very small and it was therefore not further considered. Measurements were done with fields of about 5.5 T.

The mcd spectra of the monovalent ions are shown in Fig. 1. The absorption spectra have been reproduced for comparative purposes. Except for rather minor differences, the mcd spectra of both ions are indeed mirror images. From the mcd spectra the values of B were determined with a moment analysis. These values are listed in Table I.

LCAO–SCF–MO calculations were carried out in order to compute the transition energies, dipole strengths, and mcd parameters. The parameters used

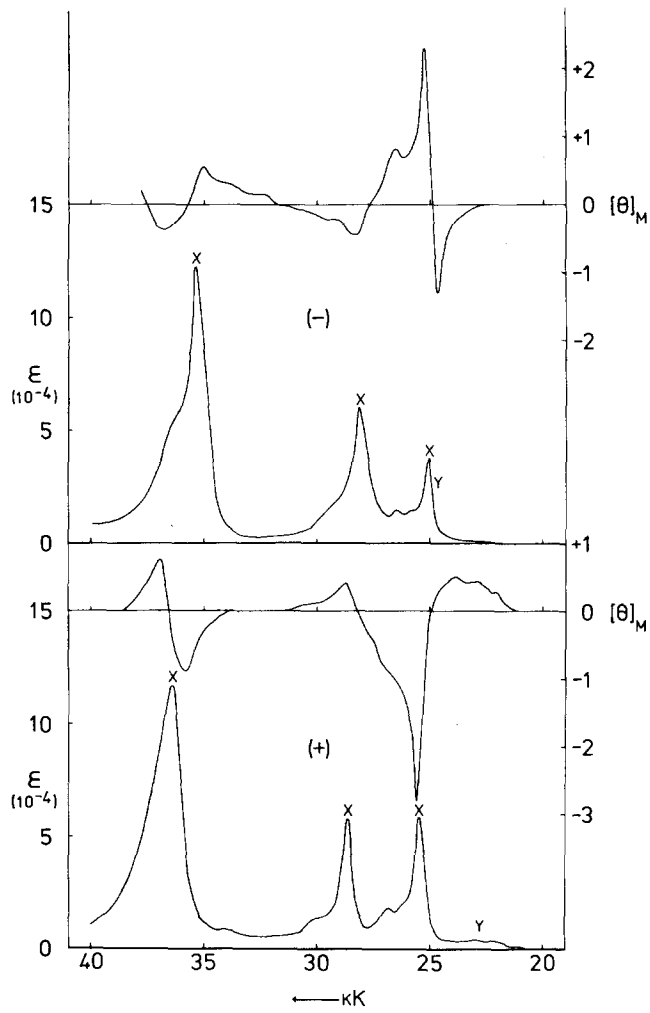

FIG. 1. Mcd and absorption spectra of tetracene monovalent ions, measured at room temperature. Top: negative ion, bottom: positive ion. Units: ϵ in $mol^{-1}\,l\,cm^{-1}$ $[\Theta]_M$ in deg $dm^{-1} \cdot mol^{-1}\,dl\,G^{-1}$.

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TABLE I. Experimental and calculated transitions. Wavenumbers (ν in kK), dipole strengths (D in Debye^2), and mcd parameters (B in Bohr magneton Debye^2 cm^{-1}) for tetracene ions. The polarizations refer to the short and longer axis y, x of the ion.

	ν		D		$B(\times 10^3)$			Pol.
	exp	calc	exp	calc	exp	calc	calc (PPP)	
1+	11.6	11.9		7.1				y
	13.3	13.2		41.6				x
	23	25.1	4.7	10.7	−1.54	−8.12	−7.98	y
	25.4	28.1	24.8	41.7	4.47	10.8	10.7	x
	28.7	28.7	22.1	11.3	−0.61	1.51	1.45	x
		33.8		0.0				y
	36.6	34.5	58.5	56.7	0.50 −0.87	−3.72	−3.72	x
1−	12.3	11.9		7.1				y
	14.3	13.2		41.6				x
	24.7	25.1	17.3	10.7	1.70	7.57	7.98	y
	25.1	28.1		41.7	−3.94	−10.2	−10.7	x
	28.2	28.7	30.8	11.3	1.09	−13.8	−1.45	x
		33.8		0.0				y
	35.3	34.5	58.9	56.7	−0.87 0.36	3.49	3.72	x

for the calculations were: resonance integral −2.2 eV, bond lengths 1.39 Å, and an ionization potential of −11.22 eV. Matago–Nishimoto repulsion integrals were used. Only singly excited configurations with energies of up to 6 eV from the ground state were considered. For both ions the same paired configurations were always taken. No attempt was made to optimalize the MO calculations since it was felt that these methods generally yield a crude estimate of the B terms, anyway (see Table I).

In the negative ion, mcd reveals the presence of a band at 24.7 kK, which has been predicted theoretically (25.1 kK, Y polarized) but which has not been found in the absorption spectrum. The overlap with the X polarized band measured at 25.1 kK (calculated 28.1 kK, X polarized) is quite large, and the experimental B values probably have a much larger magnitude than mentioned.

For the band measured at 28.2 kK, which is X polarized, the calculated B value of -1.38×10^{-3} disagrees with the experimental one of $+1.09\times 10^{-3}$. The broadness of the band which is invisible in the absorption spectrum, suggests overlap so that a positive B is found. Around 35.3 kK, two mcd bands with opposite B are observed. Measurements at low temperature (−100 °C) show that the value of 3.59×10^{-4} belongs to the large absorption band. The other band with negative B (positive Θ_M) is due to some other cause, for which our MO calculation offers no explanation.

For the positive ion, the results are similar. The experimental B values are, within a factor of two, opposite and equal to those for the negative ion. Using the PPP approximation, with neglect of nonnearest neighbor terms in the calculation of the angular momentum, one obtains exactly the same magnitudes, as predicted from theory.[2] Contrary to the case of perylene, the two neighboring bands calculated at 25.1 and 28.1 kK do not mutually induce each others B terms to a large extent.

[1]See, for instance J. Koutecky, J. Chem. Phys. 47, 1501 (1967).
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Nonadditivity extension of the Kirkwood–Buff surface tension formula

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Recent calculations[1,2] of the surface tension γ of liquid Ar near the triple point, based on Fowler's step-function density profile, have yielded good results for γ but very poor values for the surface energy U_s. The latter disagreement with experiment has suggested that the good values for γ may be due to cancellation of errors, one associated with the step-function assumption and the other with the neglect of nonadditivity effects.[2]

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